PHOTOCATALYSIS OF GLYCEROL OVER Pt/TiO_2 CATALYST

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ABSTRACT

Glycerol is produced as waste by-product in solution form during the transesterification process and potentially detrimental to the environment. Hence, photocatalysis was employed in the current work for the treatment of glycerol waste using UV light activated Pt/TiO_2 photocatalyst. The reaction was carried out under ambient conditions. The experimental work was devided into (i) preparation and characterization of the catalyst and (ii) photoreforming reaction. 5% Pt/TiO_2 was prepared. From the X-Ray diffraction analysing, the XRD pattern of the Pt/TiO2 was essentially similar to that of TiO2 sample (anatase type). The absence of diffraction lines of Pt phase on the 5% Pt/TiO2 catalyst indicates that platinum was well dispersed in the crystalline matrix. The specific surface area for 5% Pt/TiO2 is 23.60m^2/g and for TiO2 is 12.92m2/g. It was recorded 80% improvement in Pt-doped TiO2 catalyst analysed by using BET. The effects on the glycerol concentration show that when the concentration increased, the absorption of uv-light was decreased. From the kinetic study, the reaction determined was zero-order reaction with the -k value is equal to 9.5. The rates of glycerol converted to syngas were shown in the results of COD analysing. Through this research, the result obtained shows the photodecomposition of glycerol occurred under uv-light.

FOTOPEMANGKIN GLISEROL TERHADAP PEMANGKIN Pt/TiO_2

ABSTRAK

Gliserol dihasilkan sebagai sisa buangan daripada produk dalam bentuk larutan dan berpotensi untuk memudaratkan alam sekitar. Oleh itu, fotopemangkinan telah digunakan dalam proses rawatan sisa gliserol menggunakan cahaya UV dan diaktifkan oleh pemangkin Pt/TiO_2. Tindak balas dilakukan pada keadaan persekitaran. Eksperimen terbahagi kepada dua fasa iaitu (i) penyediaan dan pencirian pemangkin dan (ii) tindak balas kajian. Pemangkin 5% Pt/TiO_2 telah dihasilkan. Hasil daripada analisis pembelauan X-Ray, corak XRD Pt/TiO_2 yang pada dasarnya serupa dengan sampel TiO_2. Ketiadaan garis pembelauan fasa Pt pada pemangkin 5% Pt/TiO_2 menunjukkan platinum telah berjaya tersebar dalam matriks kristal. Luas permukaan bagi pemangkin 5% Pt/TiO_2 adalah 23.60m^2/g manakala bagi TiO_2 adalah 12.92m^2/g. Ini telah mencatatkan peningkatan sebanyak 80% apabila Pt didopkan pada TiO_2 dan dianalisa menggunakan BET. Kesan daripada kepekatan gliserol menunjukkan penyerapan cahaya UV menurun apabila kepekatan gliserol bertambah. Hasil daripada kajian menunjukkan ianya tindakbalas kosong dan nilai *–k* adalah bersamaan 9.5. Kadar gliserol ditukarkan kepada gas telah direkod dalam analisis COD. Melalui kajian ini, keputusan yang diperolehi menunjukkan penguraian gliserol berlaku di bawah cahaya UV.

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INTRODUCTION

1.1 Background of Study

Biodiesel appears to offer a means of reducing both net carbon dioxide emissions and air pollution. However, one of the issues with this technology is that for every tonne of biodiesel generated, a further 100 kg of glycerol is produced in liquid waste from which has an adverse effect on biodiesel economics (Dasari et al., 2005).

Glycerol with high purity is an important industrial feedstock for applications in food, cosmetics and pharmaceuticals, and other industries. However, it is costly to refine crude glycerol, especially for medium and small sized plants. Therefore many researchers focused on innovative usage of glycerol.

Among many possible uses for glycerol, hydrogen production from glycerol is the most attractive as demand for hydrogen as an energy carrier is expected to increase significantly in the near future as a result of the envisaged transition from a fossil-fuel-

powered economy toward a hydrogen powered one (Veziroglu et al., 1998). Hydrogen is a storable, clean, and environmentally friendly fuel. Significantly, hydrogen can be produced via photo-reforming, hence providing clean treatment of glycerol liquid waste whilst generating glycerol solution.

Douette et al. (2007)'s approach was to use nickel reforming catalyst at ca. 800°C, generating hydrogen and carbon dioxide. Whilst the lab experiment came close to generating the expected seven moles of hydrogen for each mole of glycerol the high temperature involved are far from ideal and catalyst poisoning was also an issue.

Alternatively, photocatalysis is an approach that can overcome the issue of high temperatures and appear to avoid catalyst poisoning. In the present work, the potential of photocatalysis reforming of glycerol solution waste over TiO_2 catalyst was studied. Titanium dioxide (TiO_2) has received particular attention during the past three decades as environmental friendly and low cost method for water and air purification as well as for the production of hydrogen via splitting water. It is also known to be an efficient method for reforming methanol and other alcohols in the presence of water under ambient temperatures, (Matsuoka M et al., 2005).

1.2 Problem Statement

In recent years, search for the development of biodiesel as alternative to non-renewable energy resources has become imperative. It is forecast that biodiesel could make up as

much as 20% of all transportation fuels by 2020. As biodiesel production increases exponentially, the crude glycerol produced by the transesterification of vegetables oils is also produced in a plethora amount.

There has been considerable interest in the production of biodiesel from the transesterification (exchanging the organic group R" of an ester with the organic group R' (alcohol) of oil from plants such as rape, soya and palm as a replacement for petroleum diesel. Current concerns over finite natural oil reserves and the impending consequences of global warming have led to a considerable increase in the attention given to this area.

Biodiesel appears to offer a means of reducing both net carbon dioxide emission and air pollution. The pertinent issue is the co-production of glycerol as a side product during biodiesel generation. This has an adverse effect on biodiesel economic. To enhance the economic value chain, glycerol can be converted into useful chemical compounds such as hydrogen or syngas.

1.3 Objectives

The objectives of this research are;

i. To explore the potential use of photoreforming of glycerol waste (by-product of biodiesel).

ii. To investigate the effectiveness of the synthesized photocatalyst.

1.4 Scopes of study

Following are the scopes of this research work;

i. Synthesis and physico-chemical characterization of fresh and used photocatalyst.

ii. To study the effect of glycerol concentration on photo-treatment.

iii. To obtain the kinetic parameter.

1.5 Rational & significance

The abundance of the side product in biodiesel production requires green waste conversion approach because the waste is obviously a cheaper residue for potential clean fuel production. In particular, the glycerol liquid waste can be converted into more useful material such as hydrogen production during the treatment of the waste. Hence, it will value-add the entire economic of biodiesel industry.

CHAPTER II

LITERATURE REVIEW

2.1 Glycerol

Since the energy crisis in 1970, there has been considerable interest in the production of biodiesel from the transesterification of oils from plants such as rape, soya and palm as a replacement for petroleum diesel. Current concerns over finite natural oil reserves and the impending consequences of global warming have led to a considerable increase in the attention given to this area. Biodiesel appears to offer a means of reducing both net carbon dioxide and air pollution. However, one of the issues with this technology is that for every tonne of biodiesel generated, approximately 100 kg of glycerol is produced which has an adverse effect on biodiesel economics. Hence there is a genuine need to identify new routes to convert glycerol by product into useful materials (Dasari et al., 2005).

Glycerol is the simplest trihydric alcohol as shown in Figure 2.1. It is considered to be a derivative of propane and is also known as 1,2,3-propanetriol. It is colorless,

viscous at room temperature, and odorless in pure form, has a warm sweet taste and is neutral to indicators. Its chemical formula $C_3H_8O_3$ indicates a molecular weight of 92.09, and its structural formula shows it to have two primary and one secondary hydroxyl groups.

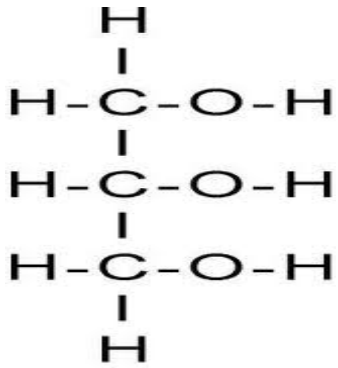

Figure 2.1 Structure of glycerol

The hydroxyl hydrogen is replaceable by metals to form glyceroxides, by acid groups to form esters and by alkyl and aryl radicals to form ethers. Its chemical nature is that of the alcohols, but because of the multiple hydroxyl groups, it possesses possibilities for more than the usual number of reactions and derivatives. The primary hydroxyls are usually more reactive than the secondary group, and the first one to react does so more readily than the second. Although one hydroxyl may be more reactive than another, there is generally some reaction of the second and third hydroxyls before all of the most reactive ones have been utilized. Consequently, glycerol derivatives are obtained as mixtures containing isomers and products of different degrees of reaction. The relative amounts of the several products reflect their ease of formation. As a result of their receptivity, the synthesis of many different derivatives is possible.

Glycerol can theoretically yield eleven oxidation products containing the original three-carbon chain. All of these compounds have been isolated and identified, but in some cases they are prepared by indirect methods rather than by direct oxidation of glycerol.

Glycerol is stable at atmospheric oxygen under ordinary conditions but is readily oxidized by some rather oxidants. The stronger oxidants carry the reaction to completion, forming CO_2 and water. These reactions are the basis of several methods for the quantitative determination of glycerol (MINER, 1953).

One possibility, recently studied by Douette et al. (2007) is the conversion of glycerol to hydrogen. The demand for hydrogen as an energy carrier is expected to increase significantly in the near future as a result of the envisaged transition from a fossil-fuel-powered economy toward hydrogen-powered one (Veziroglu et al., 1998). Hydrogen is a storable, clean, and environmentally friendly fuel, the combustion of which results in the generation of water only, with no emissions of atmospheric pollutants, greenhouse gases or particulates. However, about 95% of hydrogen is currently derived from fossil fuels, mainly by steam reforming of natural gas and petroleum (Rostrup-Nielsen et al., 2004) and, therefore, it is clearly not sustainable. Consequently, there have been intensive efforts toward the development of novel technologies for the production of hydrogen from renewable resources, mainly water and biomass (Turner et al., 2004).

These include photoelectrochemical, photocatalytic, photobiological, and enzymatic approaches, as well as steam reforming of biomass components in the gas or liquid phase and biomass gasification, which are relatively complex and energy intensive due to high temperature or pressure requirement.

2.2 Photocatalysis

Photocatalysis is an alternative approach to the conversion of glycerol which overcomes the issue of high temperatures and appears to avoid catalyst poisoning. It has recentlybecome a common word and various products using photocatalytic functions have been commercialized. Among many candidates for photocatalysts, TiO_2 is almost the only material suitable for industrial use at present and also probably in the future. This is because TiO_2 has the most efficient photoactivity, the highest stability and the lowest cost. More significantly, it has been used as white pigment from ancient times, and thus, its safety to humans and the environment is guaranteed by history. There are two types of photochemical reaction proceeding on a TiO_2 surface when irradiated with ultraviolet light. One includes the photo-induces redox reactions of adsorbed substances, and the other is the photo-induced hydrophilic conversion of TiO_2 itself. The former type has been known since the early part of the 20^{th} century, but the latter was found only at the end of the century. The combination of these two functions has opened up various novel applications of TiO_2, particularly in the field of building materials.

Photocatalytic processes over irradiated semiconductor surfaces, mainly titanium dioxide (TiO_2), have received particular attention during the past three decades as environmentally friendly and low cost methods for water (Malato et al., 2002) and air (Zhao et al., 2003) purifications as well as for the production of hydrogen by splitting of water. Photocatalytic reactions are initiated by excitation of the semiconductor with light energy ($h\nu$) equal to or greater than its band gap energy (E_{bg}).

2.3 Characteristic of TiO_2

TiO_2 powders have been commonly used as white pigments from ancient times. They are inexpensive, chemically stable and harmless, and have no absorption in the visible region. Therefore, they have a white color. However, the chemical stability of TiO_2 holds only in the dark. Instead it is active under UV light irradiation, inducing some chemical reactions. Such activity under sunlight was known from flaking of paints and the degradation of fabrics incorporating TiO_2 (Keidel et al., 1929).

Scientific studies on such photoactivity of TiO_2 have been reported since the early part of the 20^{th} century. For example, there was a report on the photobleaching of dyes by TiO_2 both in vacuo and in oxygen (Doodeve et al., 1938). It was reported that UV absorption produces active oxygen species on the TiO_2 surface, causing the photobleaching of dyes. It was also known that TiO_2 itself does not change through the photoreaction, although the "photocatalyst" terminology was not used for TiO_2 in the report but called a photosensitizer.

In Japan, there were a series of reports by Mashio et al., from 1956, entitled "Autooxidation by TiO_2 as a photocatalyst (Kato et al., 1956). They dispersed TiO_2 powders into various organic solvent such as alcohols and hydrocarbons followed by the UV irradiation with an Hg lamp. They observed the autooxidation of solvents and the simultaneous formation of H_2O_2 under ambient conditions. It is interesting to note that they had already compared the photocatalytic activities of various TiO_2 powders using twelve types of commercial anatase and three types rutile, and concluded that the anatase activity of the autooxidation is much higher than that of rutile, suggesting a fairly high degree of progress of the research (Kato et al., 1964).

The problem of light-assisted water splitting has also been focused in the late 1970s with the photocatalytic approach, i.e., essentially with photoelectrochemistry but without an external circuit. Conceptually, this is similar to the process of corrosion, as being the combination of two short-circuited electrochemical reactions.

Instead, the research shifted to the utilization of the strong photoproduced oxidation power of TiO_2 for the distruction of pollutants. The first such reports were those of Frank and Bard in 1977, in which they described the decomposition of cyanide in the presence of aqueous TiO_2 suspensions.

In 1990, it was carefully determined the reasons, in collaboration with TOTO Ltd., why TiO_2 photocatalysis could not be practical technology. It is fundamentally inadequate to utilize TiO_2 photocatalysis for either energy acquisition or the treatment of huge amounts of water and or air, because light energy density is primarily low, and in

addition, TiO_2 can utilize only the small amount of UV light contained in solar light. Based on such understanding, we conceived the idea of applying photocatalysis targeting only the substances adsorbed originally on surfaces. In other words, we could take the substances existing on two-dimensional surfaces as the object of decomposition instead of those in three-dimensional spaces such as water or air. In this case, the absolute amounts of the substances decrease, and thus, the rather weak UV light existing in an ordinary environment could be sufficient light source for maintaining the TiO_2 surface clean. We thus obtained the novel concept of light-cleaning materials, which would be coated with TiO_2 film photocatalyst (Watanabe et al., 1993).

Environment pollution, including water, air and soil is becoming an increasingly serious problem today. They have been many reports aiming at applying TiO_2 photocatalysis to pollution clean-up since the 1970s. However, the purification of the three dimensional spaces by photocatalysis is much more difficult than that of the two-dimensional surface of building materials due to the following two reasons. One is that photocatalytic reactions are surface reactions and thus the reactants must be captured by the photocatalyst surface. The other is that the total amount of reactant is, in general, higher in three-dimensional spaces than on a two-dimensional surface, indicating that much more light energy is necessary for the purification of the three-dimensional space. Therefore, practical technologies have not been obtained in this field. However, we have recently succeeded in the construction of practical purification systems for wastewater from agriculture and soil polluted by volatile organic compounds (VOCs). These system based on TiO_2 photocatalysis and use only solar light (Keidel et al., 1929).

2.4 UV-light-sensitive TiO_2

The current area of interest in this field has been the modification of TiO_2 sensitive to uv-light. One approach was to substitute Cr, Fe or Ni for a Ti site (Borgarello et al., 1982). Another approach was Ti^{3+} sites by introducing an oxygen vacancy in TiO_2 (Nakamura et al., 2000). However, these approaches were not widely accepted due to the lack of reproducibility and chemical stability.

In 2001, several groups reported uv-light-sensitive TiO_2-based powders and thin films (Sakatani et al., 2001). Subsequently, nitrogen-doped TiO_2 has attracted considerable attention. In fact similar photocatalysts sensitive to visible light have already been reported in 1986 Sato et al., 1986).

2.5 Pt catalysts

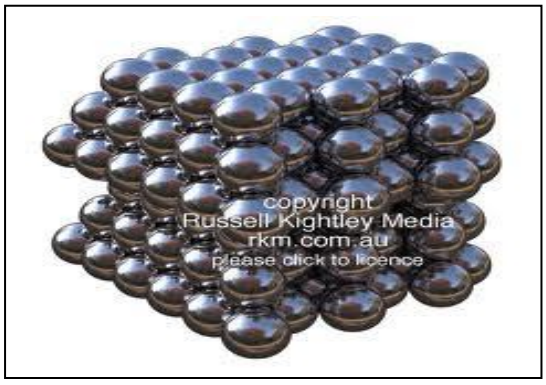

Figure 2.2 Platinum

Photocatalysis is an alternative approach to the conversion of glycerol which overcomes the issue of high temperatures and appears to avoid catalyst poisoning. In a very thorough recent paper, Kondarides reported hydrogen production by photo-reforming biomass components over Pt promoted TiO_2 catalyst (Kondarides et al., 2008).

Platinum was discovered by South American peoples who produced artifacts of a white gold-platinum alloy. The first written account of platinum was from Julius C Scaliger in 1557. He describes it as a strange metal found in mines between Panama and Mexico and wrote that no fire or any of the Spanish arts could melt it. The element name comes from the Spanish word 'platina' meaning little silver.

In 1783 Francois Chabaneaus discovered and patented a method of producing workable platinum. However the quality of the metal was still very inconsistent from batch to batch - unknown to him, there were impurities of, as then, undiscovered metals.

William H Wollaston developed a commercial process for producing pure platinum in the early 19th century. In the course of his studies on platinum ores he also discovered the metals osmium, iridium, rhodium and palladium - the elements which had made Chabaneaus' work so frustrating.

Platinum is considered to be non-toxic. It is a precious metal; soft, silvery-white, and dense with a beautiful lustrous sheen. It is malleable and ductile and has a high melting point. It also does not oxidize in air even at high temperatures and is unaffected by common acids. Platinum dissolves in aqua regia (mixture of nitric acid and

hydrochloric acid in the ratio 1:3) forming chloroplatinic acid (H_2PtCl_6) and also corroded by halogens, cyanides, sulfur, and caustic alkalis.

Platinum is widely used as a catalyst for chemical reactions. The most important use of platinum is in vehicles, as a catalytic converter, facilitating the complete combustion of unburned hydrocarbon passing through the exhaust. Platinum is used in jewelry, decoration and dental work. The metal and its alloys are also used for electrical contacts, fine resistance wires and medical / laboratory instruments. An alloy of platinum and cobalt is used to produce strong permanent magnets. The metal is also used to make electrodes sealed in glass (as its thermal coefficient of expansion is almost equal to that of glass).

Native platinum is an exotic mineral specimen and an expensive metal. Unfortunately, well formed crystals of platinum are very rare and the common habit of platinum is nuggets and grains. Pure platinum is unknown of in nature as it usually is alloyed with other metals such as iron, copper, gold, nickel, iridium, palladium, rhodium, ruthenium and osmium. The presence of these other metals tends to lower the density of platinum from a pure metal specific gravity of 21.5 to as low as 14 and very rarely any higher than 19 in natural specimens. Few of these rarer metals form significant deposits on their own and thus platinum become the primary ore of many of these metals. The presence of iron can lead to a slight magnetism in platinum nuggets and is a common enough property to be considered diagnostic.

The element platinum is extremely scarce in most crustal rocks, barely seen as even a trace element in chemical analysis of these rocks. However platinum seems to be much more concentrated in the mantle and can be enriched through magmatic segregation. Platinum's origin in the crust is from ultra-mafic igneous rocks and therefore platinum is associated with minerals common to these rocks such as chromite and olivine. Platinum's most common source however is from placer deposits.

Over the ages, the platinum became weathered out of the igneous rocks and were tumbled down streams and rivers where the extremely heavy grains and nuggets of platinum collect behind rocks and bends in the rivers and streams. These deposits, called placers, that form behind the rocks and bends are enriched in heavy grains as lighter material is carried further down stream. The heaviest grains are the nuggets of gold, platinum and/or other heavy minerals.

The metal platinum is a valuable metal that is gaining in importance. It is typically more expensive by weight than gold, mostly a product of its scarcity. Platinum is very non-reactive and for the reason it is used in chemical reactions as a catalyst. Metallic platinum can facilitate many chemical reactions without becoming altered in the process. It is also used in many anti-pollution devices, most notable is the catalytic converter, and has been given the nick name the "Environmental Metal". Native platinum is the primary ore of platinum, but deposits containing the rare platinum arsenide, sperrylite of the Pyrite Group, have made a huge contribution to the world's limited supply.

Based on what NoelKev studied, Platinum-doped titanium-dioxide/multi-walled carbon nanotubes (Pt/TiO_2/MWCNTs) composites were prepared by a sol-gel method and characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermo-gravimetry (TG) and micro-Raman spectroscopy (MRS). Regardless the nominal C/Ti molar ratio (0.3–17.0), only the anatase phase of TiO_2 was detected. However, on the composite with the highest C/Ti molar ratio, the formation of a more structurally disordered and non-stoichiometric anatase phase seemed to be favored. Small Pt nanoparticles, whose size ranged from 1 to 10 nm, were observed dispersed on the surface of composite samples. Electrical characteristics and hydrogen sensing properties of Pt/TiO_2/MWCNTs composite films deposited on inter-digitated ceramic substrates were analyzed in the temperature interval from room temperature (RT) to 100 °C. The electrical conductivity of the composite films was several orders of magnitude higher than that of pure titanium, allowing electrical measurements at RT. Pt/TiO2/MWCNTs composite films showed a response to hydrogen concentration, up to 100%, in nitrogen even at RT. On the basis of the results obtained, a "spill-over" mechanism, in which hydrogen molecules are first chemisorbed and dissociated on platinum, and finally spill out of the Pt surface, diffusing into the TiO_2 surface layer, with MWCNTs providing a preferential pathway to the current flow, can be proposed to explain the hydrogen sensing mechanism on these sensors. Pt/TiO sensing characteristics were investigated. Pt/TiO in nitrogen even at RT. A "spill-over" mechanism has been proposed to explain the hydrogen sensing on these sensors.